

CLAIMS

We claim:

1. A fluidizable catalyst comprising carbonized polysulfonated vinylaromatic polymer particles in which the particles have an average particle diameter of about 1 to about 200 micrometers ( $\mu\text{m}$ ).
2. The fluidizable catalyst as recited in claim 1 in which the particles are beads or spheres.
3. The fluidizable catalyst as recited in claim 2 in which the particles have an average particle diameter of about 5 to about 150  $\mu\text{m}$ .
4. The fluidizable catalyst as recited in claim 3 in which the particles have a BET surface area of about 100 to about 2000  $\text{m}^2/\text{g}$ .
5. The fluidizable catalyst as recited in claim 4 in which the particles have a BET surface area of about 300 to about 1500  $\text{m}^2/\text{g}$  and a pore volume ratio of about 0.5 to about 20.
6. A fluidizable catalyst comprising carbonized polysulfonated vinylaromatic polymer particles and at least one catalyst component selected from alkali metals, alkaline earth metals, metal oxides, metal hydroxides, halides, inorganic acids, and metals from Groups 4-12 of the Periodic Table of the Elements in which the particles have an average particle diameter of about 10 to about 130  $\mu\text{m}$ ; a BET surface area of about 500 to about 1200  $\text{m}^2/\text{g}$ ; and a pore volume ratio of about 0.7 to about 10.

7. The fluidizable catalyst as recited in claim 6 in which the catalyst component comprises at least one compound selected from sodium hydroxide, sodium oxide, potassium hydroxide, cesium hydroxide, barium hydroxide, barium oxide, calcium hydroxide, calcium oxide, magnesium oxide, magnesium hydroxide, hydrochloric acid, phosphoric acid, phosphomolybdic acid, or sulfuric acid.
8. The fluidizable catalyst as recited in claim 6 in which the catalyst component is one or more metals from Groups 8-12 of the Periodic Table of the Elements.
9. A fluidization process comprising i) providing to a fluidization zone a fluidizable catalyst comprising carbonized polysulfonated vinylaromatic polymer particles in which the particles have an average particle diameter of about 1 to about 200  $\mu\text{m}$  and ii) contacting the catalyst with a gas stream at a superficial gas velocity sufficient to suspend the catalyst in the gas stream.
10. The process as recited in claim 9 in which the particles have a BET surface area of about 300 to about 1500  $\text{m}^2/\text{g}$  and a pore volume ratio of about 0.5 to about 20.
11. The process as recited in claim 10 in which the superficial gas velocity is from about 0.002 cm/sec to about 3000 cm/sec.
12. The process as recited in claim 11 further comprising iii) removing a portion of the fluidizable catalyst from the fluidization zone.
13. A process for the preparation of a fluidizable catalyst comprising:
  - i) contacting vinylaromatic polymer particles having an average particle diameter of about 1 to about 200  $\mu\text{m}$  in a reaction zone with 30% oleum under sulfonation conditions of time, temperature, and pressure to produce a reaction mixture comprising polysulfonated vinylaromatic polymer particles;

- ii) washing the polysulfonated vinylaromatic polymer particles from step (i) with water; and
  - iii) heating the polysulfonated vinylaromatic polymer particles from step (ii) at a temperature from about 600°C to about 1000°C.
14. The process as recited in claim 13 further comprising:
- iv) contacting the polysulfonated vinylaromatic polymer particles from step (iii) with steam, oxygen, carbon dioxide, air, or ammonia at a temperature from about 700°C to about 1000°C.
15. The process as recited in claim 14 in which the vinylaromatic polymer particles of step i) have
- an average particle diameter of about 10 to about 130 µm;
  - a BET surface area of about 500 to about 1200 m<sup>2</sup>/g; and
  - a pore volume ratio of about 1.0 to about 8.
16. A fluidizable carbonylation catalyst comprising carbonized polysulfonated vinylaromatic polymer particles and at least one first metal selected from iron, cobalt, nickel, ruthenium, rhodium, palladium, osmium, iridium, platinum, and tin in which the particles have
- a average particle diameter of about 1 to about 200 µm;
  - a BET surface area of about 500 to about 1200 m<sup>2</sup>/g; and
  - a pore volume ratio of about 1.0 to about 8.
17. The fluidizable carbonylation catalyst as recited in claim 16 in which the first metal is rhodium or iridium.

18. The fluidizable carbonylation catalyst as recited in claim 17 further comprising at least one second metal selected from alkali metals, an alkaline earth metals, lanthanide metals, gold, mercury, vanadium, niobium, tantalum, titanium, zirconium, hafnium, molybdenum, tungsten, and rhenium.
19. The fluidizable carbonylation catalyst as recited in claim 18 in which the amount of the first metal is from about 0.01 to about 10 wt%, based on the total weight of the catalyst, and the amount of the second metal is from about 0.01 wt% to about 10 wt%, based on the total weight of the catalyst.
20. The fluidizable carbonylation catalyst as recited in claim 19 further comprising, optionally, at least one halogen promoter selected from iodine, bromine, and chlorine.
21. The fluidizable carbonylation catalyst as recited in claim 20 in which the halogen promoter is a metal halide.
22. The fluidizable carbonylation catalyst as recited in claim 21 in which the halogen promoter is sodium iodide, lithium iodide, or potassium iodide.
23. A fluidizable carbonylation catalyst prepared by a process comprising:
  - i) providing carbonized polysulfonated vinylaromatic polymer particles having an average particle diameter of about 1 to about 200  $\mu\text{m}$ ; a particle BET surface area of about 100 to about 2000  $\text{m}^2/\text{g}$ ; and a pore volume ratio of about 0.5 to about 20;
  - ii) contacting the particles in step(i) with a solution containing from about 0.01 wt% to about 20 wt%, based on the total weight of the solution, of at least one first metal selected from iron, cobalt, nickel, ruthenium, rhodium, palladium, osmium, iridium, platinum, and tin;
  - iii) drying the particles from step(ii);

24. The fluidizable carbonylation catalyst as recited in claim 23 further comprising:
  - iv) optionally, contacting the dried particles of step(iii) with a solution comprising from about 0.01 wt% to about 20 wt%, based on the total weight of the solution, of at least one second metal selected from alkali metals, alkaline earth metals, lanthanide metals, gold, mercury, vanadium, niobium, tantalum, titanium, zirconium, hafnium, molybdenum, tungsten, and rhenium;
  - v) drying the particles from step(iv);
25. The fluidizable carbonylation catalyst as recited in claim 24 further comprising the steps of:
  - vi) optionally, contacting the dried particles of step(iii) or step(v) with a solution comprising from about 0.01 wt% to about 20 wt%, based on the total weight of the solution, of a metal halide selected from sodium iodide, lithium iodide, or potassium iodide; and
  - vii) drying the particles from step(vi);
26. The fluidizable carbonylation catalyst as recited in claim 23 further comprising contacting the carbonized polysulfonated vinylaromatic polymer particles of step(i) with steam, oxygen, carbon dioxide, air, or ammonia at a temperature from about 700°C to about 1000°C.
27. A process for the preparation of a carbonylation product comprising:
  - (1) feeding a gaseous mixture comprising carbon monoxide, a carbonylatable reactant, and a halide selected from chlorine, bromine, iodine and compounds thereof to a carbonylation zone which (i) contains a fluidizable carbonylation catalyst comprising carbonized polysulfonated vinylaromatic polymer particles and at least one first metal selected from iron, cobalt, nickel, ruthenium, rhodium, palladium, osmium, iridium, platinum, and tin in which

- the particles have a average particle diameter of about 1 to about 200  $\mu\text{m}$ ; (ii) is maintained under carbonylation conditions of temperature and pressure; and
- (2) recovering a gaseous effluent comprising a carbonylation product from the carbonylation zone;
- in which the gaseous mixture of step (1) is fed to the carbonylation zone at a superficial gas velocity sufficient to suspend the carbonylation catalyst in the gaseous mixture.
28. The process as recited in claim 27 in which the carbonylatable reactant comprises at least one compound selected from methanol, ethanol, methyl acetate, and dimethyl ether.
29. The process as recited in claim 28 in which the halide comprises at least one compound selected from iodine, hydrogen iodide and methyl iodide, and the carbonylation zone is maintained at a temperature of about 100 to 350°C and a pressure of about 1 to 50 bar absolute.
30. The process as recited in claim 29 in which the first metal is rhodium or iridium.
31. The process as recited in claim 30 in which the carbonylation product comprises at least one compound selected from acetic acid, methyl acetate, and acetic anhydride.
32. The process as recited in claim 31 in which the fluidizable carbonylation catalyst further comprises at least one halogen promoter selected from iodine, bromine, and chlorine.
33. The process as recited in claim 32 in which the halogen promoter comprises at least one compound selected from sodium iodide, lithium iodide, and potassium iodide.

34. The process as recited in claim 33 in which the carbonylation catalyst further comprises, optionally, at least one second metal selected from alkali metals, alkaline earth metals, lanthanide metals, gold, mercury, vanadium, niobium, tantalum, titanium, zirconium, hafnium, molybdenum, tungsten, and rhenium.
35. The process as recited in claim 34 in which the amount of the first metal is from about 0.01 to about 10 wt%, based on the total weight of the catalyst, and the amount of the second metal is from about 0.01 wt% to about 10 wt%, based on the total weight of the catalyst.
36. A process for the preparation of acetic acid, methyl acetate, or a mixture thereof comprising:
  - (1) feeding a gaseous mixture comprising carbon monoxide, methanol, and a halide selected from iodine, hydrogen iodide, and methyl iodide to a carbonylation zone which (i) contains a fluidizable carbonylation catalyst comprising carbonized polysulfonated vinylaromatic polymer particles, rhodium, and lithium iodide in which the particles have an average particle diameter of about 1 to about 200  $\mu\text{m}$ ; (ii) is maintained at a temperature of about 150 to about 275°C and a pressure of about 3 to about 50 bar absolute; and
  - (2) recovering a gaseous product comprising acetic acid from the carbonylation zone; andin which the gaseous mixture of step (1) is fed to the carbonylation zone at a superficial gas velocity sufficient to suspend the carbonylation catalyst in the gaseous mixture.
37. The process as recited in claim 36 in which the fluidizable carbonylation catalyst has a BET surface area of about 500 to about 1200  $\text{m}^2/\text{g}$ ; and a pore volume ratio of about 1.0 to about 8.

38. The process as recited in claim 37 the gaseous mixture contains water in an amount which gives a water:methanol mole ratio of about 0.01:1 to 1:1.
39. A process for the preparation of acetic acid, methyl acetate, or a mixture thereof comprising:
  - (1) feeding a gaseous mixture comprising carbon monoxide, methanol, and a halide selected from iodine, hydrogen iodide, or methyl iodide to a carbonylation zone which (i) contains the fluidizable carbonylation catalyst as recited in claim 16; (ii) is maintained at a temperature of about 150 to 275°C and a pressure of about 3 to 50 bar absolute; and
  - (2) recovering a gaseous product comprising acetic acid from the carbonylation zone; andin which the gaseous mixture of step (1) is fed to the carbonylation zone at a superficial gas velocity sufficient to suspend the carbonylation catalyst in the gaseous mixture.
40. A process for the preparation of a hydroformylation product comprising:
  - (1) feeding a gaseous mixture comprising carbon monoxide, hydrogen, and an olefin to a hydroformylation zone which (i) contains a fluidizable carbonylation catalyst comprising carbonized polysulfonated vinylaromatic polymer particles and at least one metal selected from iron, cobalt, nickel, ruthenium, rhodium, palladium, osmium, iridium, platinum, and tin in which the particles have a average particle diameter of about 1 to about 200  $\mu\text{m}$ ; (ii) is maintained under hydroformylation conditions of temperature and pressure; and
  - (2) recovering a gaseous effluent comprising a hydroformylation product from the hydroformylation zone;

in which the gaseous mixture of step (1) is fed to the hydroformylation zone at a superficial gas velocity sufficient to suspend the carbonylation catalyst in the gaseous mixture.